

Force correlations in molecular and stochastic dynamics

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Abstract

A molecular gas system in three dimensions is numerically studied by the energy conserving molecular dynamics (MD). The autocorrelation functions for the velocity and the force are computed and the friction coefficient is estimated. From the comparison with the stochastic dynamics (SD) of a Brownian particle, it is shown that the force correlation function in MD is different from the delta-function force correlation in SD in short time scale. However, as the measurement time scale is increased further, the ensemble equivalence between the microcanonical MD and the canonical SD is restored. We also discuss the practical implication of the result.

Keywords: Brownian particle, molecular dynamics, stochastic dynamics, ensemble equivalence

1. Introduction

Since Einstein published a seminal paper on the Brownian motion in 1905, it became one of the most well-established subjects in statistical physics. The motion of a Brownian particle has been studied in many works theoretically and numerically, and was extended later to Lévy noise, Lévy flights, Lévy walks, continuous time random walks, fraction diffusion, etc. These extensions are being used to describe complex phenomena, e.g., anomalous diffusive behaviors [1] or the diffusion limited growth and aggregation mechanisms [2]. For physicists, the study of Brownian motion led to a broad class of equations of motion containing various stochastic effects. Especially, the Langevin equation [3] is the most representative differential equation with the stochastic random forces of the white noises. Mori [4] derived the generalized Langevin equation with non-Markovian noises, in which the memory kernel plays an important role. In contrast, the original Langevin equation does not have a finite memory.

Molecular dynamics (MD) [5] is a computer simulation method to describe atoms, molecules, and even stars, interacting with each others in a closed system. Since the interaction in molecular dynamics obeys classical mechanics, the positions and momenta of particles are calculated by numerical integration of Newtonian equations of motion. It is important to note that the total energy of the system in MD is conserved

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as the system moves along the trajectory in phase space. In this regard, the fundamental hypothesis of equal *a priori* probability in statistical mechanics ensures that the MD simulation basically generates the microcanonical ensemble. In the computational point of view, the number of particles in MD is often limited and far less than any real system because of the limitation in computer capacity. Even with this drawback, MD simulation has been proven to be an excellent approximation for investigation of a variety of classical quantities of real materials.

The computational limitation by the all-particle approach in the microcanonical MD can be overcome if one adopts a different approach. Imagine that we can conceptually divide the whole system into two subsystems: One is composed of the degrees of freedom we like to trace, and the other is the environment system that plays the role of heat reservoir. In the MD approach, we need to integrate all particles' equations of motion. However, if it is possible to describe interaction by environmental degrees of freedom as stochastic random forces to the system variables, numerical integrations become much lighter simply due to the reduction of the number of degrees of freedom we need to trace. In this stochastic dynamics (SD) approach, we only need to integrate equations of motion for system particles, and effects from other environmental particles are handled as stochastic random forces that satisfy some given statistical properties.

In the present work, we use the MD approach with total number N of particles, the volume V of the system, and the total energy E fixed (NVE ensemble in MD) [5]. In this MD method, it is to be noted that the time evolution of the system is deterministic and only depends on initial conditions within numerical accuracy. During the MD simulation, one is allowed to look at a single particle (call it a Brownian particle) and consider every other particles as composing an environment system, applying forces to the Brownian particle from time to time. This simple change of view allows us to make connection between the MD and the SD approaches, which composes the main theme of the present paper. In equilibrium, the energy conserving microcanonical ensemble is equivalent to the energy fluctuating canonical ensemble in thermodynamic limit [6] in most situations, with some interesting exceptions [7]. In the present context, the key question to pursue in our work is in what condition the ensemble equivalence between the MD and the SD approaches becomes valid, in parallel to the ensemble equivalence between the microcanonical and the canonical ensemble in equilibrium statistical mechanics. In more detail, we simulate the MD with the NVE ensemble and observe the motion of a Brownian particle in viewpoint of the SD. All the combined applied forces by other particles on the Brownian particle are interpreted as the effective stochastic forces, and the motion of the Brownian particle is compared with that from the simple Langevin equation with stochastic random force.

The present paper is organized as follows: In Section 2, we describe the details of our MD simulation method and quantities to be measured. The obtained results are shown in Section 3 in comparison with the SD approach of a Brownian particle, which is followed by the summary in Section 4

2. Simulation Methods

In our simulations, we use N molecules of the identical mass m in the presence of the truncated Lennard-Jones interaction called the WCA (Weeks, Chandler, and

Andersen) potential [8], which contains only the repulsive part of the Lennard-Jones interaction:

$$V_{\text{WCA}}(r) = \begin{cases} 4\epsilon \left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^6 \right] + \epsilon, & \text{for } r < r_c, \\ 0, & \text{otherwise,} \end{cases} \quad (1)$$

where $r_c \equiv 2^{1/6}\sigma$ with the interaction length scale σ and the interaction strength ϵ . This representation of potential guarantees continuity of the potential and the force at $r = r_c$, i.e., $V_{\text{WCA}}|_{r=r_c-} = V_{\text{WCA}}|_{r=r_c+} = 0$ and $(dV_{\text{WCA}}/dr)|_{r=r_c-} = (dV_{\text{WCA}}/dr)|_{r=r_c+} = 0$. We make equations of motion dimensionless by choosing σ, m, ϵ , and $\sqrt{m\sigma^2/\epsilon}$ as units of the length, the mass, the energy, and the time, respectively, and obtain

$$\ddot{\mathbf{r}}_i = 48 \sum'_{j \neq i} \left(r_{ij}^{-14} - \frac{1}{2} r_{ij}^{-8} \right) \mathbf{r}_{ij}, \quad (2)$$

where \sum' denotes that the sum is over only molecules (j 's) satisfying $r_{ij} \equiv |\mathbf{r}_{ij}| \equiv |\mathbf{r}_j - \mathbf{r}_i| < r_c$. Because the force term on the right-hand-side of Eq. (2) does not depend on the velocity, we can use the following numerical integration scheme: $v(t + \Delta t/2) = v(t - \Delta t/2) + a(t)\Delta t$ and $x(t + \Delta t) = x(t) + v(t + \Delta t/2)\Delta t$ with the position x , the velocity v , the acceleration a , and the discretized time step size Δt . This method is called the leap-frog algorithm and it is easy to see that this is the second-order algorithm although it runs at the same speed as in the simple first-order Euler method [5].

In MD simulations, a three-dimensional cubic box of the linear size L (the volume $V = L^3$) with $L = 24$ (in unit of σ) under periodic boundary condition is used. The total number of particles is set to $N = 864$ (the number density is thus fixed to $\rho = N/V = 1/16$) to make initial positions of particles fit to face-centered cubic (fcc) structure, in order to avoid the huge amplitude of the force which might happen if the particles are scattered initially at random positions. The discretized time step in numerical integration is $\Delta t = 2 \times 10^{-4}$, which is small enough so that further decrease of Δt does not change results reported in the present paper. The total simulation time is $2 \times 10^6 \Delta t = 400$. We also verify that the total energy E of the system is conserved within numerical accuracy. The total momentum should also be conserved and can be set to zero for convenience.

The equipartition theorem $(1/2) \sum_{i=1}^N m_i v_i^2 = (3/2) N k_B T$ with the Boltzmann constant k_B is used to calculate the temperature T . We first generate uniform random velocities in $[-1, 1]$ and shift them to make the total momentum (or the velocity of the center of mass) zero. The initial temperature T' is then computed from the equipartition theorem, and we scale the velocities according to $\mathbf{v}_i \rightarrow \mathbf{v}_i \sqrt{T/T'}$ to tune the system at the given temperature T . As time proceeds, the system approaches equilibrium and the temperature is computed (call it T'') again from the equipartition theorem. The deviation from the input temperature T is removed by the second velocity scaling $\mathbf{v}_i \rightarrow \mathbf{v}_i \sqrt{T/T''}$. After this procedure, we confirm that the temperature does not deviate much from the input temperature T . In our NVE ensemble MD simulations, the temperature is the control parameter and we use $T = 1, 2, 3, 4, 5$ and 6 in units of ϵ/k_B . It is then straightforward to numerically integrate the equations of motion (2) and all the presented results are obtained from the average over 100 independent runs. The key

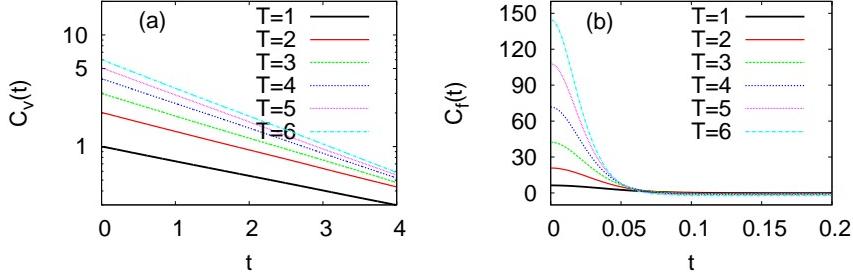


Figure 1: (a) The velocity $C_v(t)$ and (b) the force $C_f(t)$ autocorrelation functions versus time t . The velocity autocorrelation $C_v(t)$ decays exponentially in time in accord with the result from the Langevin equation for a Brownian particle. [Note that $C_v(t)$ in (a) is in the log scale]. In (b), $C_f(t)$ crosses the horizontal axis at the cutoff time t_c . The friction coefficient γ_v is computed from $C_v(t)$ via the Einstein approach, which is then compared with the friction coefficient γ_f from $C_f(t)$ (see text and Table 1).

quantities we measure during simulation is the force \mathbf{f}_i [the right-hand-side of Eq. (2)] and the velocity \mathbf{v}_i , which are then used to compute the velocity and the force auto-correlations defined by $C_v(t) \equiv \langle v_i^{(\alpha)}(t') v_i^{(\alpha)}(t' + t) \rangle$ and $C_f(t) \equiv \langle f_i^{(\alpha)}(t') f_i^{(\alpha)}(t' + t) \rangle$, respectively, with $i = 1, 2, \dots, N$, $\alpha = x, y, z$, and $\langle \dots \rangle$ being the average over particles (i), directions (α), and time (t'), after a sufficiently long equilibration time (see Fig. 1).

Before we delve into the interpretation of our MD results, we briefly review the Einstein approach for the stochastic Langevin equation of a Brownian particle [3, 9]: $m\ddot{\mathbf{r}} = -\gamma\dot{\mathbf{r}} + \boldsymbol{\eta}$, where m is the mass of the particle, γ is the coefficient of the viscous friction, and $\boldsymbol{\eta}$ is the stochastic random force assumed to be Gaussian white noise. In the same dimensionless units as in our MD, the Langevin equation is written as

$$\ddot{\mathbf{r}} = -\gamma\dot{\mathbf{r}} + \boldsymbol{\eta}, \quad (3)$$

with γ and $\boldsymbol{\eta}$ are in units of $\sqrt{m\epsilon/\sigma^2}$ and ϵ/σ , respectively, and thus the noise correlation takes the form of

$$\langle \boldsymbol{\eta}^{(\alpha)}(t') \boldsymbol{\eta}^{(\alpha)}(t' + t) \rangle = 2\gamma T \delta(t) \quad (4)$$

for each component $\alpha = x, y, z$, with T and t in units of ϵ/k_B and $\sqrt{m\sigma^2/\epsilon}$. Following the Einstein approach [3, 9], it is straightforward to calculate the velocity autocorrelation function $C_v(t) = (k_B T/m) e^{-\gamma t/m}$, which is written as

$$C_v(t) = T e^{-\gamma t}, \quad (5)$$

in our dimensionless units.

3. Results

Fig. 1(a) obtained from our MD simulation of Eq. (2) clearly shows that $C_v(t = 0) = T$ and that $C_v(t)$ decays exponentially in time, which are in perfect agreement with the result from the Einstein approach in Eq. (5). A simple curve fitting of $C_v(t)$ to the exponential function gives us the friction coefficient γ_v (we use the subscript v

Table 1: Friction coefficients computed from the velocity autocorrelation and the force autocorrelation functions [γ_v and γ_f in Eqs. (5) and (6), respectively] at various temperatures T . The time integration of the correlation function $G_{MD}(t)$ for the MD in Eqs. (8) and (9) is also shown together with the cutoff time t_c defined from zero crossing of $C_f(t)$ in Fig. 1(b). The relaxation time scale τ of $G_{MD}(t)$ is also listed (see text).

T	γ_v	γ_f	t_c	$\int_0^{t_c} G_{MD}(t) dt$	τ
1.0	0.30(1)	0.30(1)	0.118	0.97(1)	0.048
2.0	0.38(1)	0.39(1)	0.096	1.00(1)	0.038
3.0	0.46(1)	0.46(1)	0.086	0.97(1)	0.033
4.0	0.51(1)	0.52(1)	0.078	0.98(1)	0.029
5.0	0.55(1)	0.57(1)	0.072	1.00(1)	0.026
6.0	0.58(1)	0.60(1)	0.068	1.00(1)	0.025

to indicate that it is computed from the velocity correlation), which are tabulated in Table 1.

Alternatively, the friction coefficient can also be found from the Green-Kubo formula for the force autocorrelation function [10, 11]:

$$\gamma_f = \frac{1}{3T} \int_0^{t_c} \langle \mathbf{f}(0) \cdot \mathbf{f}(t) \rangle dt \quad (6)$$

in dimensionless form, where 3 in the denominator comes from the dimensionality. The cutoff time t_c can be taken large enough so that the force autocorrelation function has arrived at plateau region [10]. Lagar'kov and Sergeev [12] have proposed another practical solution in which t_c is taken as the first zero of the force autocorrelation function. We use the latter approach and compute the friction coefficient γ_f based on Eq. (6) and present results in Table 1. It is to be noted that the two different ways of computing the friction coefficient, one from velocity autocorrelation and the other from force autocorrelation, give us the identical results within numerical accuracy. The agreement between γ_v and γ_f can also be interpreted as implying the ensemble equivalence between the MD and the SD, since γ_v is based on the expression from the Einstein approach for the SD, while the expression for γ_f is based on the MD.

In order to check the equivalence between the MD and the SD in more detail, we next study the force autocorrelation function. For this, we first start from Eq. (3) and write

$$\begin{aligned} \langle f(0)f(t) \rangle &= \langle [-\gamma v(0) + \eta(0)][-\gamma v(t) + \eta(t)] \rangle \\ &= \gamma^2 \langle v(0)v(t) \rangle + \langle \eta(0)\eta(t) \rangle \end{aligned} \quad (7)$$

for one direction (we have skipped the index α for direction for brevity), and the time t is measured after equilibration so that the correlation is invariant under time translation. We define another correlation function $G(t)$ as

$$G(t) \equiv \frac{\langle \eta(0)\eta(t) \rangle}{\gamma T} = \frac{\langle f(0)f(t) \rangle - \gamma^2 \langle v(0)v(t) \rangle}{\gamma T}. \quad (8)$$

In MD, we know all velocities and forces at each time, which are used to compute $G(t)$ in Eq. (8) [we call it $G_{MD}(t)$], combined with the friction coefficient computed above

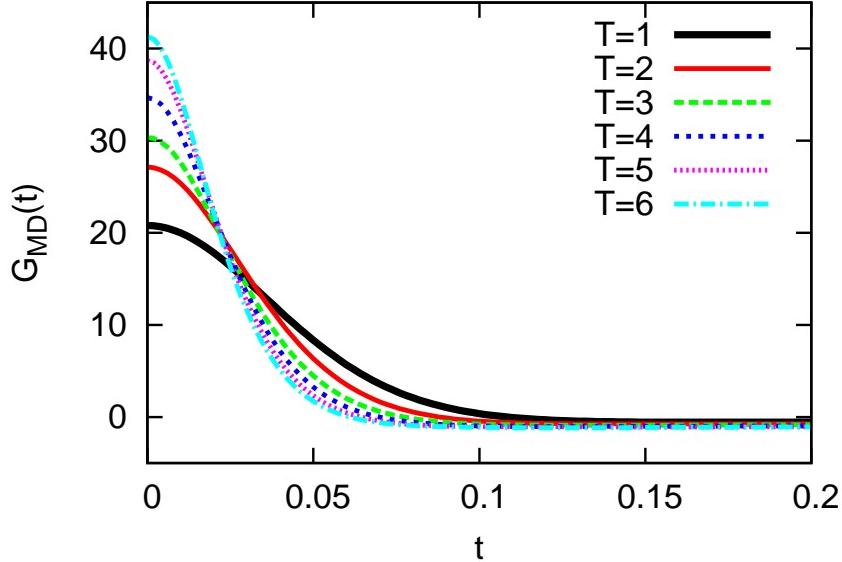


Figure 2: The correlation function $G_{MD}(t)$ versus time t in Eq. (8) calculated for the MD simulation. $G_{MD}(t)$ decays in time with finite relaxation time (see text and Table 1), which differs from $G_{SD}(t) = 2\delta(t)$.

(Table 1). On the other hand, the corresponding correlation function $G_{SD}(t)$ for SD is written as $G_{SD}(t) = 2\delta(t)$ from Eqs. (4) and (8).

Fig. 2 shows $G_{MD}(t)$ at different temperatures. The relaxation time scale τ for $G_{MD}(t)$ can be estimated by using the method in Ref. [13] with the time integration up to t_c (see Eqs. (8)-(10) in Ref. [13]). The resulting values of τ at various temperatures are tabulated in Table 1. If the observation time scale is much larger than the relaxation time scale τ of MD, we expect one can approximate $G_{MD}(t) \approx G_{SD}(t) = 2\delta(t)$. To confirm the equivalence between MD and SD in such a long-time scale, $G_{MD}(t)$ needs to satisfy

$$\int_0^{t_c} G_{MD}(t)dt = \int_0^{t_c} G_{SD}(t)dt = 2 \int_0^{t_c} \delta(t)dt = 1, \quad (9)$$

where the last equality comes from the evenness of the delta function in time, and in the same spirit as in Eq. (6) we have used t_c (see Table 1) as the cutoff of the integration in Eq. (9). We find that the equivalence between the MD and the SD is convincingly borne out as listed in Table 1, where $\int_0^{t_c} G_{MD}(t)dt \approx 1$ at all temperatures, as expected.

In comparison to the MD, the use of SD has a significant benefit in practical point of view due to the small number of degrees of freedom to integrate. The key question to answer is then what is the condition for the equivalence between the MD and the SD. We find above that the observation time scale must be sufficiently large so that the correlation function $G_{MD}(t)$ can be approximated as a delta function as in $G_{SD}(t)$ to see the consistency between the SD and the MD: if we are only interested in long-time behavior, it is reasonable to use the SD instead of the MD. In other words, although the

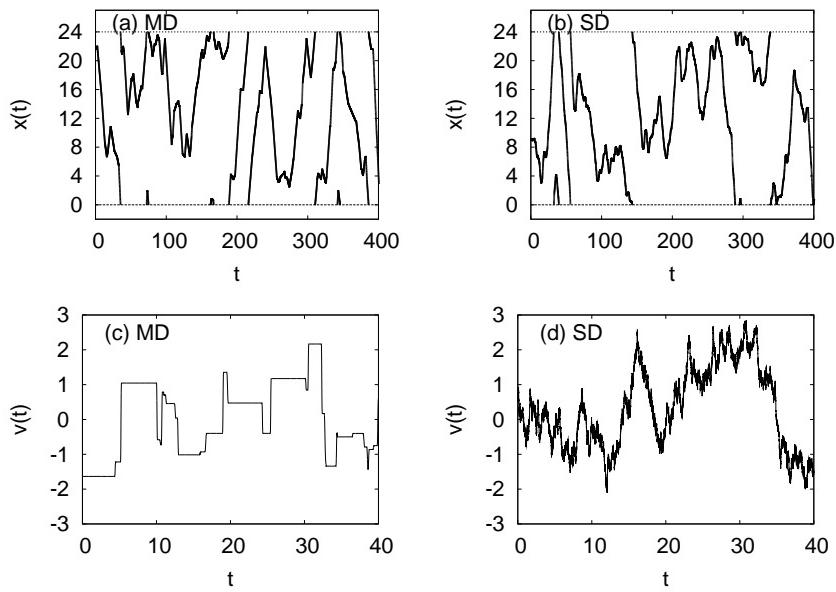


Figure 3: The position of a particle in x direction versus time t is shown for (a) the MD and (b) the SD in a long-time scale of $O(10^2)$. (c) and (d) display the velocity $v(t)$ for the MD and the SD, respectively, in a shorter-time scale of $O(10)$. When the observation time scale is long enough, trajectories from the MD and the SD are qualitatively the same [see (a) and (b)]. On the other hand, in a shorter-time scale, they behave very differently [see (c) and (d)].

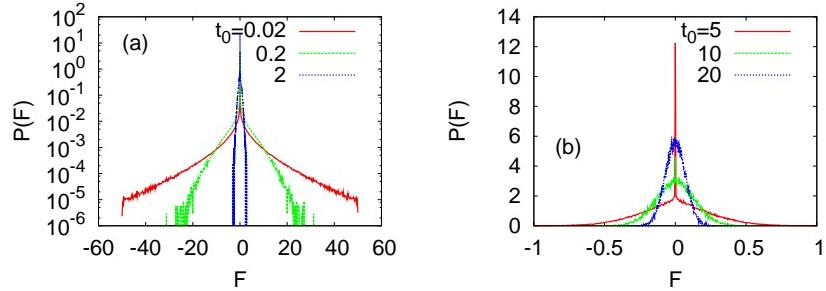


Figure 4: The probability density function $P(F)$ for the time averaged force F for the time interval t_0 . As t_0 is increased [from (a) to (b)], $P(F)$ approaches the Gaussian form, again implying the ensemble equivalence between the MD and the SD.

motion of the particle in the MD in short-time scale is very different from that of the simple Langevin dynamics, the two cannot be distinguished in long-time scale.

Fig. 3 displays trajectories $x(t)$ for (a) the MD and (b) the SD at the same temperature $T = 1$ in a long-time scale. In our SD simulation, we integrate the equation of motion for a Brownian particle by using the Runge-Kutta second-order algorithm with the same discrete time step $\Delta = 2 \times 10^{-4}$ in dimensionless time unit. As expected, the two trajectories look qualitatively the same. In contrast, $v(t)$ in a shorter-time scale for (c) the MD and (d) the SD look quite different: for MD with the WCA potential, particles interact only when the distance between them is smaller than r_c , and thus $v(t)$ changes in time in a step-like fashion. The ensemble equivalence between the MD and the SD in a long-time scale displayed in Fig. 3 can also be seen in the probability density function $P(F)$ for the time-averaged force F in Fig. 4, where $F(t) \equiv (1/t_0) \int_t^{t+t_0} f(t') dt'$. As the measurement time scale t_0 becomes larger, $P(F)$ approaches the Gaussian distribution, again revealing the ensemble equivalence between the MD and the SD in a long-time scale. The similar ensemble equivalence has also been discussed as the mass ratio between the Brownian particle and the environment particle is varied [14].

4. Summary

In summary, we have studied the gas system with the WCA potential within the MD approach and compared the results with the SD based on a simple Langevin equation. The velocity and the force autocorrelation functions have been computed and a good agreement has been observed in the friction coefficient calculated independently from each correlation function. It has been revealed that as the observation time scale becomes much larger than the relevant relaxation time scale of correlation function, the ensemble equivalence between the microcanonical MD and the canonical SD approaches is established. It is to be noted that the present study and the results are limited by the relatively low particle density. As the particle density is increased, the system will become liquid-like. In this liquid regime, the autocorrelations become more extended in time, and the generalized Langevin formulation with memory needs to be used.

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